研究简报

二维 Hofmann 类双金属配合物 Cu(DMF)₂[Pt(CN)₄]的合成及晶体结构

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Synthesis and Crystal Structure of a Two-Dimensional Hofmann-Type Bimetallic Complex Cu(DMF)₂[Pt(CN)₄]

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Abstract: A two-dimensional cyanide-bridged Cu(II)-Pt(II) bimetallic complex has been synthesized by solution diffusion method using $[Pt(CN)_4]^{2-}$ and $[Cu(L)]^{2+}$ (L=3,10-diethanol-1,3,5,8,10,12-hexaazacyclotetradecane) as building blocks. Unexpectedly, the obtained complex Cu(DMF)₂[Pt(CN)₄] (**1**) is an analogue of the well-known Hofmann-type clathrate without macrocyclic ligand. Single-crystal X-ray diffraction reveals that **1** crystallizes in monoclinic, space group $C2/m$, a=1.624 8(6) nm, b=0.739 3(3) nm, c=0.695 5(3) nm, β=108.969(4)°. The crystal structure of **1** consists of two-dimensional corrugated metal cyanide sheets without interpenetration stacking along the a axis in an ABAB packing mode. CCDC: 756100.

Key words: cyanide-bridged; macrocyclic ligand; Hofmann-type; crystal structure

0　Introduction

Coordination polymers have attracted much interest because of their multi-functional properties[1-4]. Cyano-bridged metal complexes are among the first coordination complexes but are still extensively investigated in recent years for their unique magnetic[5-6], spin-crossover[7-9], catalytic[10], host-guest[11], gas-storage[12-13] and negative thermal expansion properties[14-15]. One strategy to assemble 1D, 2D and 3D coordination polymers is to combine cyanometalates building blocks such as $[M(CN)_4]^{2-}$ (M=Ni, Pd, and Pt), $[M(CN)_6]^{3-}$ (M= Fe, Mn, Cr and Co) and $[M(CN)_8]^{3-/4-}$ (M=Mo, W and Nb) with mononuclear complexes containing macrocyclic ligands[16-18]. Cyanometalates exhibit bridging character involving either one or several of the cyano groups and can construct various coordination polymers with different structural topologies. Macro-cyclic ligands usually occupy several coordination sites of the metal ions and leave axial sites available for cyano groups.

Herein, we chose $[Pt(CN)_4]^{2-}$ and $[Cu(L)]^{2+}$ (L=3,10-diethanol-1,3,5,8,10,12-hexaazacyclotetradecane) as

building blocks and attempt to construct a new cyano-bridged coordination polymer containing macrocyclic ligand. However, an unexpected two-dimensional Hofmann-DMF-type complex $Cu(DMF)_2[Pt(CN)_4]$ (**1**) without macrocyclic ligand was obtained instead.

1　Experimental

1.1　Materials and physical measurements

All chemicals and solvents in the synthesis were of reagent grade and used as received. $[Cu(L)](ClO_4)_2$ were synthesized as described in the literature[19]. Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled in small quantities with great care. Elemental analyses for C, H, and N were carried out with a Perkin-Elmer 240C analyzer.

1.2　Synthesis

Well-shaped bright green-blue crystals of **1** suitable for X-ray single-crystal structure determination were grown at room temperature by slow diffusion of a DMF solution (2 mL) of $[Cu(L)](ClO_4)_2$ (0.05 mmol) and an aqueous solution (20 mL) of $K_2[Pt(CN)_4] \cdot 3H_2O$ (0.05 mmol) for about 3 weeks. The resulting crystals were collected, washed with H_2O and dried in air. Yield 30%. Anal. Calcd. for $C_{10}H_{14}N_6PtO_2Cu$ (%): C 23.60, H 2.77, N 16.51; Found(%): C 23.52, H 2.78, N 16.48.

1.3　X-ray crystallography

Diffraction data for **1** was collected at 173(2) K on a Bruker Smart Apex Ⅱ CCD diffractometer with graphite monochromatic Mo $K\alpha$ radiation (λ =0. 710 73 nm) using the φ-ω scan mode. Diffraction data analysis and reduction were performed within SMART and SAINT[20]. Correction for Lorentz, polarization, and absorption effects were performed within SADABS [21]. Structures were solved using Patterson method within SHELXS-97 and refined using SHELXL-97[22]. All non-hydrogen atoms were refined anisotropically. The sites of hydrogen atoms were placed by the geometry. The C (H) atoms of the DMF ligand were placed in calculated position and refined using a riding model, with $U_{iso}(H)$= $1.5U_{eq}(C)$. Selected crystal data collection and refinement parameters are given in Table 1.

CCDC: 756100.

**Table 1　Data collection and structure refinement for 1**

Formula	$C_{10}H_{14}CuN_6O_2Pt$
Formula weight	508.9
Crystal system	Monoclinic
Space group	$C2/m$
a / nm	1.624 8(6)
b / nm	0.739 3(3)
c / nm	0.695 5(3)
β / (°)	108.969(4)
V / nm³	0.790 1(6)
Z	2
D_c / (g·cm⁻³)	2.139
Crystal $F(000)$	478
μ (Mo $K\alpha$) / mm⁻¹	10.198
Total / unique data	3 340 / 965
Observed data [$I>2\sigma(I)$]	965
R_{int}	0.037 4
R_1, wR_2 [$I>2\sigma(I)$]	0.020 3, 0.045 6
R_1, wR_2 (all data)	0.020 3, 0.045 6

2　Results and discussion

2.1　Crystal structure

ORTEP and packing diagrams of **1** are shown in Fig.1 and Fig.2, respectively. Selected bond lengths and bond angles are given in Table 2. The crystal structure of **1** consists of two-dimensional corrugated metal cyanide networks (Fig.2a). The similar corrugated
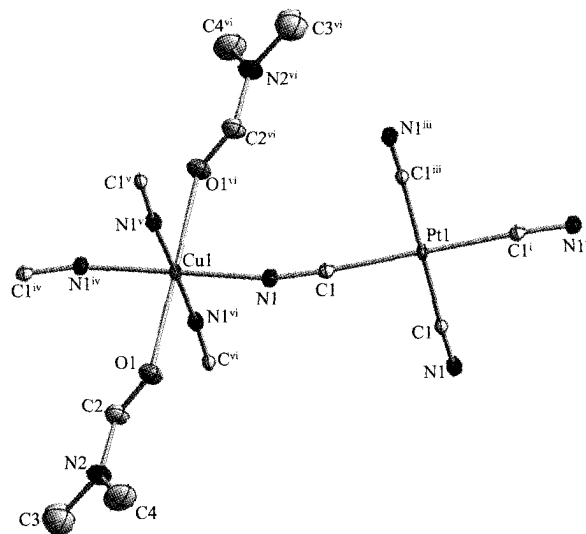
Symmetry codes: ⁱ $-x$, $-y+1$, $-z+2$; ⁱⁱⁱ $-x$, y, $-z+2$; ⁱᵛ $-x$, $-y$, $-z+1$; ᵛ x, $-y$, z; ᵛⁱ $-x$, y, $-z+1$

Fig.1　ORTEP diagram of **1**, Displacement ellipsoids are drawn at the 30% probability level and H atoms are omitted for clarity

polymeric sheets are also reported in some related complexes with H_2O molecules as the axial ligands[23-25]. The network is formed with linkages of cyanide between Cu and Pt centers. In the structure, the [Pt(CN)₄] moiety has a square planar geometry with four bridging cyano ligands. The coordination sphere of Cu center is six-coordinated by four cyano nitrogens and two oxygen atoms from two DMF ligands, describing a slightly distorted octahedral geometry. The equatorial coordination sites of Cu atom are occupied by four N atoms from the bridging cyano groups, whereas two O atoms from two DMF ligands are in the axial positions. The DMF molecules, bound to the Cu atom in *trans* position, are located on both sides of the network planes (Fig.1). The average Cu-N and Cu-O bond lengths are *ca.* 0.199 4(3) nm and 0.236 4(4) nm, respectively. The Pt-C-N bond is nearly linear with the bond angle of 176.2(3)°.

As displayed in Fig.2b, the two-dimensional sheets of **1** are square grid-like networks and the length of side is *ca.* 0.51 nm (Cu···Pt distance). In addition, these sheets stack together in an ABAB packing mode along the *a* axis without interpenetration. The distance between the adjacent A and B sheets is *ca.* 0.772 8 nm (Cu···Pt distance), while the offset distance between the adjacent sheets is *ca.* 0.25 nm (about the half distance of Cu···Pt) in the *bc* plane.

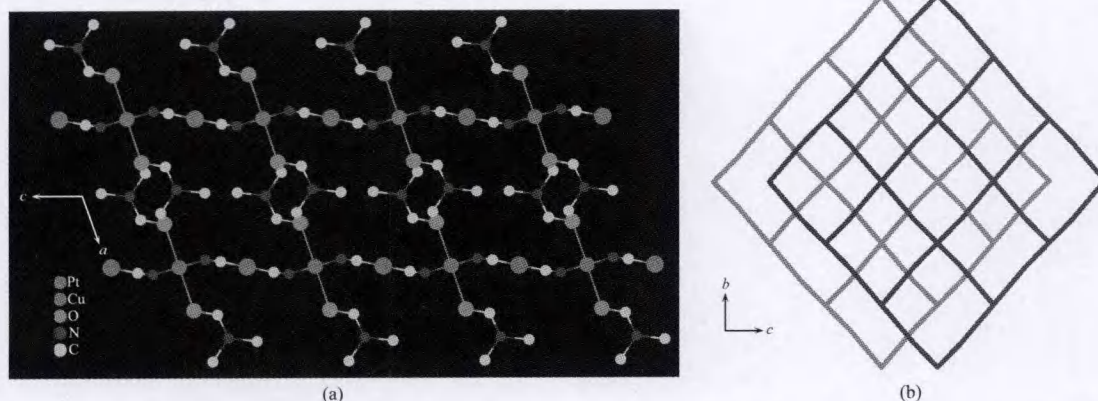Fig.2   View of the stacking without interpenetration of sheets along the *a* and *b* axis of **1**

Table 2   Selected bond lengths (nm) and angles (°)

Cu(1)-N(1)	0.199 4(3)	Pt(1)-C(1)	0.198 6(3)	Cu(1)-O(1)	0.236 4(4)
N(1)-C(1)	0.115 5(5)				
C(1)-Pt(1)-C(1)	88.64(1)	N(1)-Cu(1)-O(1)	88.13(1)	C(1)-N(1)-Cu(1)	164.5(3)
N(1)-Cu(1)-N(1)	88.83(1)	O(1)-Cu(1)-O(1)	180.0	N(1)-C(1)-Pt(1)	176.2(3)

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